

Final Report

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Nitric Oxide Photolysis

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The major findings of the project relative to the photolysis of nitric oxide in the three far-ultraviolet regions around 1600 Å, 1470 Å and 1236 Å were published in the Journal of Chemical Physics 42, 2107, March 15, 1965. Reprints of this article form part of this report.

There remains only to add to the article a report on the problem of nitrous oxide which the mass-spectrometric analysis indicated present in the photolysis products at 1470 Å but not at 1600 Å, not at 1236 Å. Reports on nitrous oxide as a product are conflicting in the earlier literature, while the presence of nitrogen atoms together with nitrogen dioxide, postulated in the mechanism of the photolysis, should, according to previous reports in the literature produce nitrous oxide. The problem is one of analysis. The molecular weight of nitrous oxide is 44, as is that of carbon dioxide. Although, with the use of pure reactants, carbon dioxide could not be present among the actual products of photolysis, nevertheless, nitrogen dioxide, a product, can oxidize carbon in the filament of the ion source of the spectrometer, the filaments usually being drawn through diamond dies, to yield carbon dioxide. In an attempt to recognize nitrous oxide in the presence of carbon dioxide, the mass-spectrometric analysis reported in the reprint, had used the double ionized carbon dioxide value at 22 as its measure, subtracting this amount from the total reading at 44, the difference taken as nitrous oxide. Since, in any case, the amount of nitrous oxide is very small, the precision of its measure is poor, as the small difference of the two larger quantities, carbon dioxide alone and carbon dioxide plus nitrous oxide.

The experimental evidence for nitrous oxide production from nitrogen atoms and nitrogen dioxide by Kistiakowsky, depends on the same analysis and Kistiakowsky's paper reports his skepticism concerning the analysis even after "conditioning the mass-spectrometer for a long time." In the studies on the reaction of nitrogen atoms with ozone, Taylor and Chen reported the presence of nitrous oxide and attributed it to this reaction. Later, Schiff reports that nitrous oxide is not produced and attributes our findings to carbon dioxide. It was apparent that a new analytical procedure was required. Several attempts have been made in various laboratories around the country to analyze mixtures of the oxides of nitrogen by gas chromatography. Several techniques of procedure have been reported. There is, however, conflict among the claims. Some insist on a preliminary fractionation, particularly of the nitrogen dioxide.

Others have claimed this unnecessary. Obviously it would be necessary to develop a technique, reproducible perhaps only for an individual technician, since none of the mixtures reported having been analyzed, contained the minute amounts believed to be present in our systems. After carefully testing suggested techniques the following procedure was adopted.

An Aerograph (Model A-90-P2) gas chromatograph of the Wilkens Instrument Co. was used with a General Electric 0-1 millivolt range recorder. The adsorbent was a six inch column of silica gel (30-60 mesh) and was used at room temperature with helium as the carrier gas at flow rates in the range of 60-65 ml/min. The sensitivity of the instrument was increased by increasing the size of sample injected to 20 ml., increasing the cell current to 190 m.a. and removing a 220 ohm shunt resistor on the D. C. terminal strip. Samples were injected using a gas-sampling valve connected directly to a vacuum system, pressures being measured on an octoil manometer.

In elution, N_2 , NO and NO_2 were removed in the first ten minutes and N_2O around twenty minutes. The NO and NO_2 peaks were not always separable, the one appearing as a shoulder on the other peak at some concentrations but the retention of the N_2O permitted easy separation and therefore recognition. By calibrating standard mixtures of N_2 , NO, NO_2 and N_2O , a lower limit for the detection of N_2O was established at 10^{-8} mole.

Some twenty photolyses of NO at 1470 Å were made and the products analyzed by the new procedure. None of these showed any N_2O . Since there appeared to be some small variation in the retention time of N_2O from sample to sample of the calibrating standards, the photolysis product analysis was sandwiched between two standard runs. No N_2O peak appeared. In an effort to increase the concentration of NO_2 with which N atoms might react during photolysis, small amounts of oxygen were added to the NO before photolysis. Still no N_2O could be found. Finally, small amounts of N_2O were added initially to the NO and the mixture photolyzed at 1470 Å. The products after the run contained no N_2O . It is apparent that during the period of the photolysis any N_2O that might be produced was decomposing.

It is to be concluded that the N_2O , suspected in the earlier work reported in the accompanying reprint, was actually CO_2 and that under the experimental conditions with a duration of photolysis of from 15 to 20 minutes no N_2O is present among the final products.

While definitely answering the question of the presence of N_2O in the system studied earlier, it must be realized that another question is posed in its place, namely, if the duration of the photolysis were shortened, could N_2O be found among the products before its decomposition. F. O. Rice and F. J. Wunderlich have recently published a Communication in the Journal of Physical Chemistry, 69, 2137 (1965) on the photolysis of nitrogen dioxide with radiation predominantly 3655 Å using a flow method with exposure times of $10 - 140 \times 10^{-5}$ min. They find N_2O a major product together with O_2 and NO , and postulate as an intermediate an excited N_2O_3^* formed from excited NO^* and NO_2 . They present evidence that their radiation contained some mercury resonance radiation, presumably 2536 Å, which produced a photosensitized N_2O decomposition. Their results consequently are minimum values for N_2O , but in addition the excited NO^* is produced also by mercury photosensitization.

Although this recent work is on a system far from a parallel to our system in that the excitation in our system is to much higher states, there may remain some analogy. To investigate this, as well as to attempt to answer the question of the effect of a change in the duration of photolysis, the research assistant, Mr. Sethi, has undertaken as his doctoral problem, NO photolysis at 1470 Å by a flow method. This work will probably continue during this academic year. After making, as rapidly as possible for the purposes of this report, the transition from the former static system to a flow system and using the gas-chromatographic analysis method, he has shown in two preliminary runs, with contact times of the order of 1 min. that N_2O is produced. He proposes to follow this as a function of contact time with the possibility of distinguishing between the reaction of NO_2 with either NO^* or N atoms. The results cannot affect markedly the conclusions of the accompanying paper for the conditions therein studied. Suffice to say, however, that the last word on NO photolysis in the far U-V is still to be said.

The Director wishes to express his deep appreciation to the National Aeronautics and Space Administration for the assistance that has made this project possible.